

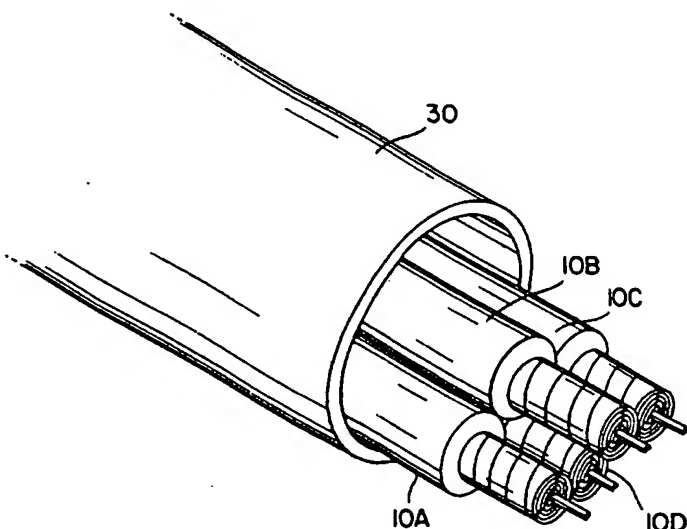
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



76

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : G02B 6/22, 6/36, 6/44		A1	(11) International Publication Number: WO 95/11472
			(43) International Publication Date: 27 April 1995 (27.04.95)
(21) International Application Number: PCT/US94/09423			(81) Designated States: AU, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 18 August 1994 (18.08.94)			Published With international search report.
(30) Priority Data: 136,839 18 October 1993 (18.10.93) US			
(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).			
(72) Inventors: ASHJIAN, Henry; 22 Surrey Lane, East Brunswick, NJ 08016 (US). SHEN, Dong-Ming; 508 Fawn Hill Drive, Langhorne, PA 19047 (US). WU, Margaret, May-Som; 45 Richmond Drive, Skillman, NJ 08558 (US).			
(74) Agents: SUNG, Tak, K. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).			
(54) Title: FIBER OPTIC CABLE AND VISCOUS FILLER MATERIAL			
			
(57) Abstract			
<p>The invention provides a fiber optic cable (10) comprising an optical fiber (12) and the grease (14) applied over the optic fiber (12). Surrounding grease (14) is a sheath (16). Additional layers of grease (18 and 22) may optionally be applied in sequence with outer sheaths (20 and 24), if desired. Furthermore, the invention provides a fiber optic cable (10) and a diamondoid-based viscous filling material for a fiber optic cable (10).</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

FIBER OPTIC CABLE AND VISCOUS FILLER MATERIAL

This invention relates to an optic fiber cable and a viscous filler material useful in the manufacture and installation of optic fiber cables.

5 Fiber optics have been in use for many years, in applications such as medical endoscopes, cathode ray tube faceplates, flexible light distribution bundles, automobile indicator lamps, and borescopes, which require light transmission of a few meters at most. More recently, fiber
10 optics have entered the telecommunication field, transmitting signals over distances several orders of magnitude longer. For a survey of the development of fiber optics, see 10 Kirk-Othmer Encyclopedia of Chemical
15 Technology 125 et seq. (3rd ed., 1980).

15 U.S. Patents 4,441,787 to Lichtenberger and 4,653,851 to Pedersen et al. teach fiber optic cables and methods for manufacturing the same. U.S. Patent 4,749,059 to Jonnes et al. teaches a cable lubricating device useful for applying grease to a fiber optic cable.

20 U.S. Patent 4,602,763 to Gaylin discloses a method for drawing a fiber optic cable through a conduit.

 U.S. Patent 4,688,890 to DeMeo et al. relates to a fiber optic cable innerduct for containing and protecting fiber optic cable and for reducing the drag on fiber optic
25 cable as it is pulled through the innerduct.

 The fiber optic cables used commercially typically comprise an inner optic fiber surrounded by a protective sheath. The optic fiber is typically lubricated, and the outer shell of the protective sheath may also be lubricated
30 to reduce friction when drawing the assembly through a conduit for installation. Proper lubrication between the optic fiber and the protective sheath helps to minimize microbending and the concomitant signal loss. Further, the cushioning effect of a viscous lubricant renders the optic
35 cable assembly more resistant to impact damage. See the

Lichtenberger '787 patent at column 2, lines 26-69, and also column 5.

The telecommunications industry needs optic cable assemblies which can be easily installed (e.g., buried
5 underground) and then operated for decades without maintenance. Thus the cable filler material or lubricant must not only be thermally and oxidatively stable, but must also be inert to the cable sheath material. Additionally, the cable filler material should be resistant to
10 biodegradation. The optic cables should also be suitable for installation and use over a wide range of temperatures, particularly in cold winter conditions. The goals of lubricant inertness (including thermal and oxidative stability, as well as resistance to biodegradation) and
15 substantially constant viscosity and lubricity over a broad range of temperatures have, in the past, been in conflict because lower molecular weight solvents (which tended to deteriorate the cable sheath material) were required to attain the desired low temperature viscosity and lubricity
20 characteristics.

Efforts to improve upon the performance of natural mineral oil based lubricants by the synthesis of oligomeric hydrocarbon fluids have been the subject of important research and development in the petroleum industry for at
25 least fifty years and have led to the relatively recent market introduction of a number of superior polyalpha-olefin synthetic lubricants, primarily based on the oligomerization of alpha-olefins or 1-alkenes. In terms of lubricant property improvement, the thrust of the
30 industrial research effort on synthetic lubricants has been toward fluids exhibiting useful viscosities over a wide range of temperature, i.e., improved Viscosity Index, while also showing lubricity, thermal and oxidative stability and pour point equal to or better than mineral oil. To match
35 synthetic lubricants with their intended application, these lubricants have, in the past, been formulated for specific

properties. For example, poly-alpha-olefins (PAO) were produced from 1-decene polymerization over promoted BF₃ or AlCl₃ catalysts. While poly-alpha-olefins are useful components in fiber optic cable filler materials, it would
5 be desirable to provide fiber optic cable filler materials with still further improved lubricity, oxidative stability, thermal stability, and resistance to biodegradation over a broad range of temperatures.

The invention provides, in a first aspect, a fiber
10 optic cable assembly comprising:
(a) at least one optical fiber;
(b) a sheath longitudinally surrounding and substantially concentric with the optical fiber;
(c) a grease in contact with the optical fiber and the
15 sheath, the grease comprising at least 70 weight percent diamondoid-containing compounds, of which diamondoid compounds at least 65 weight percent are alkyl-substituted diamondoid compounds, and a thickener component which is substantially inert to
20 the sheath.

The diamondoid component of the grease preferably contains at least 65 weight percent of diamondoid compounds which have more than one quaternary carbon atom per molecule and less than 35 weight percent of diamondoid
25 compounds which have less than two quaternary carbon atoms per molecule. The grease preferably comprises at least 75 weight percent diamondoid-containing compounds, more preferably at least 80 weight percent or more of diamondoid-containing compounds.

30 The invention provides, in a second aspect, a grease composition comprising a diamondoid component comprising at least 65 weight percent alkyl-substituted diamondoid compounds which have more than one quaternary carbon atom per molecule and less than 35 weight percent of diamondoid
35 compounds which have less than two quaternary carbon atoms

per molecule; and a thickener component which is substantially inert to a fiber optic cable sheath.

The diamondoid component of the grease for the invention preferably contains less than 1 weight percent non-hydrocarbons. Examples of diamondoid compounds which contain more than one quaternary carbon include 1,3-dimethyladamantane; 1,3,5-trimethyladamantane; 1,3,5,7-tetramethyladamantane; cis- and trans-1,3,4-trimethyladamantane; 1,2,5,7-tetramethyladamantane; 4,9-dimethyldiamantane; 1,4-dimethyldiamantane; 2,4-dimethyldiamantane and 3,4-dimethyldiamantane. The diamondoid component of the grease of the invention preferably contains more than 80 weight percent of diamondoid compounds having more than one quaternary carbon atom per molecule and less than 20 weight percent of diamondoids having fewer than two quaternary carbon atoms per molecule.

The diamondoid component of the grease of the present invention comprises a diamondoid-based composition which:

(a) is substantially inert to commonly used cable sheath materials; (b) has an unusually high Viscosity Index; (c) maintains its thermal and oxidative stability, as well as its chemical inertness to commonly used sheath materials, over extended periods of time, i.e. decades.

In a third aspect, the present invention provides a fiber optic cable grease comprising a diamondoid component containing at least about 10 different diamondoid compounds selected from methyl-substituted and ethyl-substituted adamantane, diamantane, triamantane, and higher homologs, wherein each of the selected diamondoid compounds comprises no more than 10 weight percent of the diamondoid component; and a second component comprising a thickener which is substantially inert to common fiber optic cable sheath materials, e.g. Kevlar brand aramid fiber manufactured by E.I. DuPont de Nemours and Company of Wilmington, Delaware. This diamondoid component of the second fiber optic cable

grease composition of the invention is similarly characterized by unusually high Viscosity Index (typically exceeding about 100) and very low pour point.

In a preferred embodiment, the third aspect of the invention includes a diamondoid component comprising at least 15 different diamondoid compounds selected from methyl-substituted and ethyl-substituted adamantane, diamantane, and triamantane, wherein each of the selected diamondoid compounds comprises no more than 7 weight percent of the composition. The composition preferably comprises from 30 to 70 weight percent substituted and unsubstituted adamantanes, from 20 to 60 weight percent substituted and unsubstituted diamantanes, and from 3 to 20 substituted and unsubstituted triamantanes. The composition may optionally comprise less than about 10 weight percent of adamantanes, diamantanes, or triamantanes.

The Viscosity Index for the diamondoid component of the grease compositions of the present invention consistently exceeds 100. In preferred embodiments, the Viscosity Index of the diamondoid component of the grease compositions of the present invention exceeds 110, and in a particularly preferred embodiment the Viscosity Index exceeds about 115. The diamondoid-based component of the grease composition of the invention may be produced by mixing individual diamondoid components, by blending mixtures of diamondoids, by fractionating and treating a naturally occurring diamondoid mixture, or by selectively alkylating diamondoids with selected olefins. U.S. Patent 5,120,899 to Chen and Wentzek teaches a method for recovering a diamondoid-containing mixture from a natural gas stream.

The diamondoid component of the grease composition of the invention typically contains less than 10 weight percent C_9 - components, preferably less than 5 weight percent C_9 - components. The first preferably contains less

-6-

than 5 weight percent aromatics, and more preferably less than 1 weight percent aromatics. The composition preferably contains a minimum of color bodies (also referred to as colorants) and may be treated with a sorbent
5 such as activated carbon or activated alumina to remove such compounds. In a particularly preferred embodiment, the diamondoid component is substantially free of C₆-components, particularly C₆-aromatics.

The diamondoid component of the grease composition of
10 the invention is most preferably used neat to maintain its superior thermal and oxidative stability, but may be blended, if desired, with a synthetic or petroleum-based lubricant stock. Examples of useful synthetic lubricant blending stocks are taught in U.S. Patents 4,943,383 to
15 Avery et al., 4,952,303 to Bortz et al., 4,962,249 to Chen et al., 4,967,029 to Wu, 4,967,032 to Ho et al., 4,990,709 to Wu, 4,990,718 to Pelrine, 4,990,238 to Cruzman et al., 4,992,189 to Chen et al., 4,995,962 to Degnan, Jr., et al.,
20 5,012,020 to Jackson et al., 5,015,795 to Pelrine, 5,068,046 to Blain et al., and 5,095,165 to Hsia Chen. These patents are incorporated herein for teaching synthetic lubricant blending components.

The diamondoid component of the grease composition of the invention may suitably comprise a major portion of
25 diamondoid compounds, for example, at least 80 weight percent. The diamondoid component preferably contains at least 90 weight percent diamondoid compounds and more preferably contains 98 weight percent or more of diamondoid compounds. The diamondoid component of the grease
30 typically contains at least 65 weight percent alkyl-substituted diamondoid compounds.

The composition of the invention behaves in an unusual and surprising manner at low temperatures. Specifically,
the composition of the invention can be distilled to remove
35 lower-boiling components without significantly increasing its freeze point. This unusual characteristic is of

critical importance to its properties as a viscous filler material or grease for fiber optic cables. The composition of the invention is generally characterized by a freeze point of less than -40°C .

5 In one preferred embodiment, the diamondoid component of the grease composition of this invention comprises diamondoid compounds having at least one unsubstituted bridgehead hydrogen which have been selectively alkylated with at least one C_6+ α -olefin in the presence of an acidic
10 catalyst selected from the group consisting of AlX_3 and BX_3 , wherein X is a halogen, and in the absence of an added active proton-containing additive. The term "active proton-containing additive" as used herein refers to active proton-containing compounds such as water, alcohols, and
15 HX , wherein X is a halogen, which compounds can readily release a proton. Selectively alkylating diamondoid compounds with an α -olefin in the absence of an added active proton-containing additive avoids substantial self-polymerization of the α -olefin alkylating agent. This
20 selectively alkylated diamondoid mixture is more fully disclosed in U.S. Application Serial No. 08/070,823, filed June 3, 1993, (Mobil Docket 7065).

In another preferred embodiment, the diamondoid component of the grease composition of this invention
25 comprises alkyl-substituted adamantanes wherein the ratio of linear to branched alkyl substituents is at least 1:1, preferably at least 4:1, and wherein the average number of alkyl substitutions per diamondoid molecule is from 1.5 to 4. The lubricant composition of the invention is generally
30 characterized by a Bromine Number (prior to hydrogenation) of less than about 13, preferably less than about 5. This selectively alkylated diamondoid mixture is more fully disclosed in U.S. Application Serial No. 08/070,815, filed June 3, 1993, (Mobil Docket 7068).

35 Figure 1 is a simplified diagram showing an embodiment of the fiber optic cable of the invention.

Figure 2 is a simplified diagram showing fiber optic cables of the invention in a conduit.

Referring now to Figure 1, a fiber optic cable in accordance with the present invention is shown at 10. An
5 optic fiber 12, suitable for use as an optical waveguide extends along the axis of the cable. During manufacture of the cable, the grease of the present invention 14 is applied over the optic fiber. Note that grease film thicknesses in Figure 1 are not shown to scale.
10 Surrounding grease 14 is sheath 16. Additional layers of grease, 18 and 22, may optionally be applied in sequence with outer sheaths 20 and 24, if desired.

The sheath material should be flexible, lightweight, and of high tensile and flexural strength. Kevlar 49, an
15 aramid fiber manufactured by E.I. DuPont de Nemours and Company is the preferred sheath material. The Kevlar sheath is helically wound upon the grease coated optical fiber. Similarly, if additional sheaths are desired, the grease of the present invention may be applied to the
20 underlying sheath material and the next concentric sheath is wound upon the previous grease coated sheath. For a detailed description of a useful manufacturing method for the fiber optic cable of the present invention, see U.S. Patent 4,441,787 to Lichtenberger at column 4, line 8 et
25 seq. For cable lubricating means, see U.S. Patent 4,749,059 to Jonnes et al., which teaches a cable lubricating device useful for applying grease to a fiber optic cable.

Figure 2 shows four (4) optical cables of the type
30 illustrated in Figure 1, 10A through 10D, which are encased in a conduit 30. The grease composition of the present invention may suitably be applied to the outer sheath (shown as reference numeral 24 in Figure 1) of each optic cable before it is drawn through the conduit during
35 installation. Because the grease of the present invention retains its viscosity and lubricity over a broad range of

temperatures, installations need not be limited to moderate temperature conditions to assure effective lubrication during the cable drawing procedure, and may be conducted during extreme cold conditions as low as -40°C. For a
5 general description of optic cable drawing, see U.S. Patent 4,602,763 to Gaylin.

In one embodiment of the grease composition, preparing the diamondoid component of the grease requires no chemical conversion steps but is restricted to processing via
10 selective separation for example, removal of light (C₃-) hydrocarbons and non-hydrocarbons. Examples of non-hydrocarbons include polar sulfur and nitrogen compounds or polar corrosion inhibitors which may be injected upstream in the natural gas production equipment as well as
15 naturally occurring color bodies. Examples of such useful sorptive media include gamma-alumina, activated charcoal, sand, and clay, merely to name a few. The diamond compound-containing mixture may optionally be hydrotreated to reduce total sulfur and/or to improve color.

20 The diamondoid component of the grease composition of the invention may be further processed (e.g., distilled) while maintaining substantially constant freeze point. The diamondoid component of the grease composition of the invention exhibits unusual freeze point behavior upon
25 distillation. Distilling the diamondoid component of the grease composition of the invention to remove lower boiling fractions does not significantly increase the freeze point of the mixture. Previously known compositions compromised thermal and oxidative stability, as well as inertness, to
30 meet a freeze point specification by blending a viscous lubricant component with a low freeze point diluent such as cyclohexane. The composition of the present invention requires no such compromise. This behavior stands in marked contrast to that of previously known viscous
35 lubricant mixtures which require the addition of a low freeze point diluent.

In accordance with the present invention, it was found that the thermal and oxidative stability of certain diamondoid mixtures may be easily converted into thermally and oxidatively stable grease components by percolation through a suitable medium to sorb impurities such as polar sulfur and nitrogen compounds or polar corrosion inhibitors. Examples of such sorptive media include gamma-alumina, activated charcoal, sand, and clay, merely to name a few. The sorption step may be used in conjunction with a distillation step to adjust the composition of the diamondoid component as needed.

The sorption step may suitably be conducted at ambient temperature and atmospheric pressure, but may also be conducted under elevated conditions of temperature and pressure. For example, suitable temperature for the sorption step range from 20 to 50°C, and suitable pressures range from atmospheric to 805 kPa (about 100 psig).

The diamondoid component of the grease composition of the invention may optionally be treated under hydrogen pressure in the presence of a hydrotreating catalyst of the type typically used in the petroleum refining industry for desulfurization, denitrogenation, and demetallation of hydrocarbonaceous feedstocks.

Suitable catalysts include metals on an inert or catalytically active support as a heterogeneous catalyst. Useful heterogeneous catalysts may contain metals from Groups IVA or VIIIA of the Periodic Table of the Elements, published by Sargent-Welch of Skokie, Illinois (catalog no. S-18806). Sulfides and oxides of these metals are also useful catalyst components. Specific examples of useful metals, metallic oxides and sulfides within these groups are exemplified by sulfides and oxides of Ni, Mo, W, Co, Pt, Pd, Cu, and Cr. Bimetallic catalysts including Ni-Mo, Ni-W, Co-Mo, and Cu-Cr are particularly preferred.

Both inert and catalytically active binders may be employed, with examples including one or more of alumina,

-11-

silica, silica-alumina, zeolites, clays, Kieselguhr, and active carbons from sources such as coal, coke, and coconut shell.

5 The above-listed metals may also be exchanged onto zeolites to provide a zeolite catalyst having dehydrogenation activity. Suitable zeolites include those commonly referred to as large pore, i.e., those zeolites having a Constraint Index of less than about 1, such as zeolite X, and zeolite Y as well as those commonly referred
10 to as medium-pore, i.e., those zeolites having a Constraint Index of from about 1 to about 12. Examples of suitable medium-pore zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, and ZSM-48. Zeolite Beta, known to exhibit characteristics of either a large pore zeolite or a medium-
15 pore zeolite, is also useful in the present invention.

The zeolite-containing catalysts useful in the hydrotreating process of the present invention more preferably include those catalysts which exhibit Constraint Indices of from 0.1 to 10, for example ZSM-5, MCM-22 and
20 Zeolite Beta, although it is well recognized that the Constraint Index of zeolite Beta varies widely with temperature. Zeolite Beta is described in U.S. Patents 4,696,732; 3,308,069, as well as Re. 28,341.

A convenient measure of the extent to which a zeolite
25 provides control to molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. The method by which the Constraint Index is determined is described in U.S. Patent Number 4,016,218. U.S. Patent Number 4,696,732, cited above, discloses Constraint Index
30 values for typical zeolite materials.

Zeolite ZSM-5 and the conventional preparation thereof are described in U.S. Patent Number 3,702,886. Other preparations for ZSM-5 are described in U.S. Patent Numbers Re. 29,948 (highly siliceous ZSM-5); 4,100,262 and
35 4,139,600. Zeolite ZSM-12 and the conventional preparation thereof are described in U.S. Patent Number 3,832,449.

-12-

Catalysts such as ZSM-5 combined with a Group VIII metal described in U.S. Patent No. 3,856,872 are also useful in the present invention.

Additional catalytic materials useful in the present invention include materials which are readily identified by their characteristic X-ray diffraction patterns, such as the PSH-3 composition of U.S. Patent No. 4,439,409, incorporated herein by reference, and MCM-22, the synthesis and composition of which is taught in U.S. Patent 4,954,325, both of which patents are incorporated by reference as if set forth at length herein.

The optional hydrotreating step may suitably be conducted under the conditions listed below in Table 1.

TABLE 1

Hydrotreating Reaction Conditions		
<u>Process Variable</u>	<u>Broad</u>	<u>Preferred</u>
Temperature, °C	30-220	50-180
WHSV, based on catalyst	0.01-100	0.1-5
Pressure, kPa	100-14,000	170-7000
Hydrogen Dosage, Mols H ₂ /Mol diamondoid mixture	0.05-100	1-10

The grease composition of the invention comprises a thickener which is substantially inert to the fiber optic cable sheath. Examples of useful grease thickeners include those taught in U.S. Patents 4,961,868, 5,068,045, and 5,084,194, each to Doner, Horodysky, and Keller. For a general survey of useful grease thickeners, see Klamann, Lubricants 389-422 (1984). Examples of useful thickeners (colloidal fillers) for optic fiber cable greases are also taught in U.S. Patent 4,810,395 to Levy et al. at column 4, line 33, through column 5 at line 30. Specific examples of useful thickeners include colloidal silica, fatty acid soaps, clays, bentonites, styrene-rubber or styrene-rubber-styrene block copolymers, as well as semi-liquid rubbers,

such as polyisobutylene, merely to name a few. Colloidal silica is preferred, and a hydrophobic fumed silica having a BET surface area between 50 and 400 m²/g is more preferred. Cab-O-Sil N70-TS brand fumed silica produced by the Cabot Corporation of Tuscola, IL, is a particularly preferred thickener.

Thickener dosage typically ranges between 3 and 20 wt% of the total grease composition, usually from 6 to 10 wt%, and preferably from 6 to 7 wt%.

10

Examples

Examples 1-10 illustrate diamondoid mixtures useful in the grease composition of the present invention. Compositions for Examples 1, 2, and 4 are shown in Table 2, while Table 3 shows properties of the diamondoid mixtures.

15

EXAMPLE 1

A raw diamondoid-containing fluid was distilled to remove the light end. The residual liquid was further treated to remove any color components in the product by passing the liquid through an activated alumina column at room temperature.

20

EXAMPLE 2

Example 1 was repeated except the distillation was carried out further to remove all adamantanes.

EXAMPLE 3

Example 1 was repeated except the distillation was carried out further to remove all adamantanes and diadamantanes.

25

EXAMPLE 4

Example 1 was repeated with a different starting diamondoid mixture.

30

-14-

EXAMPLE 5

1-Ethyl adamantane was prepared by hydrogenating 1-vinyl adamantane (M. Zuanic, et al. J. Poly. Sci. Lett. Ed. 19, 387-9, 1981) using Ni/SiO₂ catalyst at 100°C and 1400 kPa (200 psi).

EXAMPLE 6

1,3-Dimethyladamantane was obtained from Aldrich Chemical Co.

EXAMPLE 7

Decyl adamantane was prepared by reacting 140 g 1-decene, 54.4 gram adamantane in 100 cc n-hexane solvent and using 3 mmoles 1.0 M AlBr₃ in CH₂Br₂ or AlBr₃ catalyst at 15-50°C reaction temperature. The product was isolated by quenching the catalyst with dilute acid and aqueous work-up followed by distillation at 155°C and 0.2 mm-Hg using a Kugelrohr to remove any C₂₀-material. The C₃₀+ fraction was obtained in 80% yeild. It was hydrogenated at 200°C and 3500 kPa (500 psi) H₂ using 1 wt.% Ni/SiO₂ catalyst.

EXAMPLE 8

Decyl (whole) diamondoid fluid was prepared by adding 300 g 1-decene to a mixture of 300 g diamondoids from Example 1, 0.50 g water, and 10.0 g anhydrous AlCl₃, maintained at 40-51°C over 8 hours. The reaction mixture was heated t 40°C for another 10 hours after finishing adding 1-decene. Following aqueous work-up, the crude product was vacuum distilled to remove low-boiling starting material and products up to a b.p. of 160°C/0.78 mm-Hg to give 449 g high boiling products. The latter was hydrogenated at 200°C and 3500 kPa (500 psi) H₂ using 1 wt.% Ni/SiO₂ catalyst.

EXAMPLE 9

Decyl adamantanes were prepared in a similar method as Example 8 except the starting diamondoid fluid contained only the adamantane fraction, which was isolated from the distillation process described in Example 2. The crude product was distilled till 158°C/0.61 mm-Hg.

EXAMPLE 10

Example 10 repeated Example 9, except the hydrogenated products were further distilled to remove lower-boiling products up to 164°C/0.65 mm-Hg.

The products in examples 1 to 6 have very high VI and low pour points. The products in examples 7 to 9 have much better thermal stabilities than the existing PAO, as indicated by much smaller amount of viscosity loss than PAO when tested at 288°C under nitrogen for 72 hours.

Table 2.

	Example 1	Example 2	Example 4
Compounds *			
adamantane	1.364	none	1.234
1-methyl adamantane	5.615	none	7.617
1,3-dimethyl adamantane	6.070	none	10.174
1,3,5-trimethyl adamantane	2.438	none	4.796
1,3,5,7-tetraamethyl adamantane	0.413	none	0.713
2-methyl adamantane	1.003	none	1.754
t-1,4-Dimethyl adamantane	1.514	none	2.980
c-1,4-Dimethyl adamantane	1.516	none	3.459
1,3,6-Trimethyl adamantane	1.774	none	4.083
1,2-Dimethyl adamantane	1.483		3.368
1r, 3,4t-Trimethyl adamantane	2.056		4.647
1r, 3,4c-Trimethyl adamantane	2.117		4.898

		Example 1	Example 2	Example 4
	Compounds *			
	1,3,5,6-tetramethyl adamantane	2.044		5.308
	1-ethyl adamantane	0.630		1.523
	2,6-; 2e,4e-; 2e,4a-diMe Ad	0.118		0.285
	1,2,3,5-tetramethyl	0.07		0.17
5	1-ethyl-3-methyl adamantane	2.16		5.17
	1,2,3-Trimethyl adamantane	0.34		0.81
	1-ethyl-3,5-dimethyl adamantane	1.582	0.012	3.909
	1-ethyl-3,5,7-trimethyl adamantane	0.424		1.031
	1,2,3,5,7-pentamethyl adamantane	1.050	0.029	2.489
10	Other adamantanes	14.432	6.631	23.083
	Total adamantanes	50.213	6.672	93.501
	Diamantane	3.967	5.560	1.342
	4-Methyl-diamantane	5.345	8.338	1.522
	4,9-Dimethyl-diamantane	1.710	2.784	0.400
15	1-Methyl-diamantane	3.343	5.664	0.624
	2,4-Dimethyl-diamantane	2.078	3.611	0.395
	1,4-dimethyl diamantane	2.563	4.509	0.406
	1,4,9-trimethyl diamantane	1.103	1.981	0.196
	3-methyl diamantane	2.384	4.241	0.359
20	4,8-Dimethyl diamantane	1.618	2.970	0.195
	4-Ethyl-diamantane	0.584	1.206	0.043
	Other diamantanes	16.597	34.282	1.017
	Total diamantanes	41.292	75.146	6.499
	Triamantane	1.175	2.608	0.017
25	9-methyl triamantane	1.151	2.583	0.016
	9,15-dimethyl triamantane	0.233	0.521	
	3-Me & 3,9-diMe triamantanes	0.696	1.560	
	7,9-diMe & 3,9,15-triMe triamantanes	0.489	1.136	

-17-

		Example 1	Example 2	Example 4
	Compounds *			
	4-Me & 4,9,15-triMe triamantanes	0.440	0.973	
	4,9- & 6,9-dimethyl triamantanes	0.184	0.419	
	5-methyl triamantane	0.289	0.661	
	5,9-methyl triamantane	0.180	0.395	
5	8-Me & 5,9,15-triMe triamantanes	0.244	0.585	
	9,14-dimethyl triamantanes	0.144	0.238	
	8,9-dimethyl triamantanes	0.069	0.210	
	16-methyl-, a diMe- & a triMe-triamantanes	0.366	0.837	
10	2-methyl triamantane	0.118	0.302	
	other triamantanes	1.857	4.402	
	Total triamantanes + methyl and dimethyl derivatives	7.605	17.430	0.033
	iso-tetramantane + A + B	0.119	0.283	
15	anti-tetramantane	0.023	0.059	
	other tetramantanes	0.139	0.410	
	Total tetramantane	0.281	0.752	0.000

¶ This sample contained 6.821 % of lower boiling materials.

- 20 * Prefixes a-, e-, c-, and t- refer to axial, equatorial, cis-, and trans- relationship of substituents in the same cyclohexane ring bearing the substituents in the diamondoids.

Table 3. Properties of Diamondoid and Alkyldiamondoids

Ex. No.	Product Type	Initial BP °C (°F)	Visc. at 100°C, cS	VI	Pour Point, °C	% Visc loss (a)
1		-204 (-400)	2.4	101	-94	
2	6:4 diamantanes: triamantanes	-343 (-650)	4.9	126	-72	
3	9:1 triamantanes: tetramantanes	-399 (-750)	9.1	103	-40	
4	Partially solid (at ambient) diamondoids	-204 (-400)	1.7	118	--	
5	1-ethyl adamantane	227 (440)	1.6	118	-58	
6	1,3-dimethyl adamantane	210 (410)	1.2	163	-29	
7	decyl adamantane	>399 (>750)	12.03	124	--	+1.4
8	decyl (whole) diamondoids	>399 (>750)	14.28	89	-37	-5.4
9	decyl adamantanes	>399 (>750)	12.38	98	-45	-13.9
10	decyl adamantanes	>399 (>750)	14.5	98	-40	--
11	Comparative PAO Sample A	>399 (>750)	5.59	131	-54	-25
12	Comparative PAO Sample B	>399 (>750)	39.11	148	-36	-30

(a) % viscosity loss was measured the viscosity loss after heating the oil to 288°C for 72 hours under nitrogen. Positive number indicated viscosity increase. Negative number indicated viscosity loss. PAO Samples A and B (Examples 11 and 12) are commercial polyalphaolefin lubricant basestocks.

The diamondoid mixtures described above exhibit lower pour points than conventional mineral oils, thus producing an optic fiber cable grease which allows the optic fiber cable to remain flexible even in extreme low temperature applications. Further, because these diamondoid mixtures have markedly higher Viscosity Indices than typical mineral oils, the grease of the present invention retains stable viscosity over wide temperature ranges. Because the

diamondoid mixtures of the invention exhibit much higher fluid densities than mineral oil or a polyalphaolefin (PAO) lubricant stock, the diamondoid mixtures of the invention more effectively suspend thickening solids and provide a
5 more homogeneous filling grease which is less susceptible to phase separation than a conventional mineral oil- or PAO-containing grease.

Changes and modification in the specifically described embodiments can be carried out without departing from the
10 scope of the invention which is intended to be limited only by the scope of the appended claims.

CLAIMS:

1. A grease composition comprising at least 70 weight percent of a diamondoid component, said diamondoid component comprising at least 65 weight percent alkyl-substituted diamondoid compounds; and a thickener component.
5
2. The grease composition of claim 1 wherein said diamondoid component of said grease further comprises at least 65 weight percent of diamondoid compounds which have more than one quaternary carbon atom per molecule and less than 35 weight percent of diamondoid compounds which have less than two quaternary carbon atoms per molecule.
5
3. The grease composition of claim 2 wherein said diamondoid component of said grease further comprises diamondoid compounds having at least one unsubstituted bridgehead hydrogen which diamondoid compounds have been selectively alkylated with at least one C₆+ α -olefin in the presence of an acidic catalyst selected from the group consisting of AlX₃ and BX₃, wherein X is a halogen, and in the absence of an added active proton-containing additive.
10
15
4. The grease composition of claim 2 wherein said diamondoid component of said grease further comprises alkyl-substituted adamantanes wherein the ratio of linear to branched alkyl substituents is at least 1:1, and wherein the average number of alkyl substitutions per diamondoid molecule is from 1.5 to 4.
20

5. A fiber optic cable grease comprising a diamondoid component containing at least about 10 different diamondoid compounds selected from the group consisting of methyl-substituted and ethyl-substituted adamantane, diamantane, triamantane, and higher homologs, wherein each of said selected diamondoid compounds comprises no more than about 10 weight percent of said diamondoid component; and a second component comprising a thickener which is substantially inert to a fiber optic cable sheath.
6. A grease composition comprising a diamondoid component comprising at least 65 weight percent alkyl-substituted diamondoid compounds which have more than one quaternary carbon atom per molecule and less than 35 weight percent of diamondoid compounds which have less than two quaternary carbon atoms per molecule; and a thickener component which is substantially inert to a fiber optic cable sheath.
7. A fiber optic cable assembly comprising:
- (a) at least one optical fiber;
 - (b) a sheath longitudinally surrounding and substantially concentric with said optical fiber;
 - (c) a grease in contact with said optical fiber and said sheath, said grease comprising a diamondoid component which has been processed to remove at least a portion of organics having fewer than 10 carbon atoms, said diamondoid component comprising at least about 65 weight percent alkyl-substituted diamondoid compounds; and a thickener component which is substantially inert to said sheath.

8. The fiber optic cable of claim 7 wherein said diamondoid component of said grease further comprises at least about 65 weight percent of diamondoid compounds which have more than one quaternary carbon atom per molecule and less than about 35 weight percent of diamondoid compounds which have less than two quaternary carbon atoms per molecule.
- 5
9. The fiber optic cable of claim 7 wherein said grease further comprises at least 70 weight percent of diamondoid compounds.
- 10
10. The fiber optic cable of claim 9 wherein said grease further comprises at least 80 weight percent of diamondoid compounds.
11. The fiber optic cable of claim 7 wherein said grease further comprises diamondoid compounds having at least one unsubstituted bridgehead hydrogen which diamondoid compounds have been selectively alkylated with at least one C₆+ α -olefin in the presence of an acidic catalyst selected from the group consisting of AlX₃ and BX₃, wherein X is a halogen, and in the absence of an added active proton-containing additive.
- 15
- 20
12. The fiber optic cable of claim 7 wherein said grease further comprises alkyl-substituted adamantanes wherein the ratio of linear to branched alkyl substituents is at least about 1:1, preferably at least 4:1, and wherein the average number of alkyl substitutions per diamondoid molecule is from 1.5 to 4.
- 25

1/1

FIG. 1

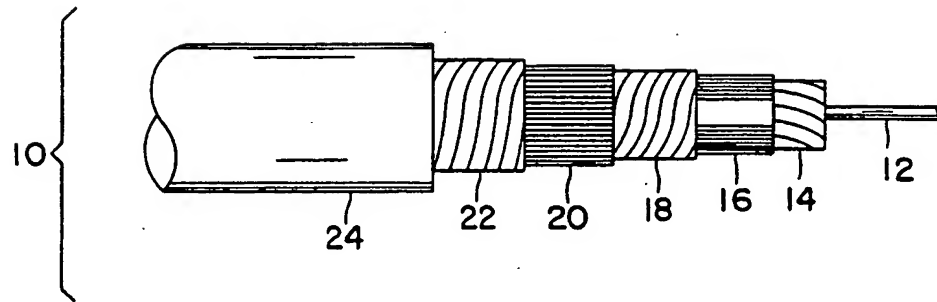
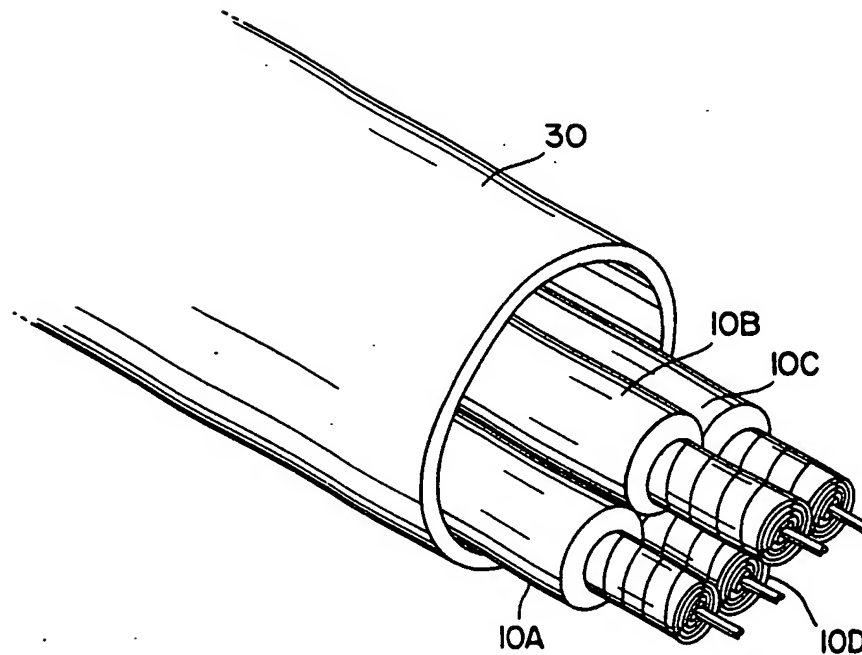


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/09423

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : G02B 6/22, 6/36, 6/44,
US CL : 385/100,101,102, 109, 113

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 385/100,101,102, 109, 113

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,053,434 (CHAPMAN) 01 OCTOBER 1992	
A	US, A, 5,019,660 (CHAPMAN ET AL.) 28 MAY 1991	
A	US, A, 4,749,059 (JONES ET AL.) 07 JUNE 1988	
A	US, A, 4,688,890 (DEMEO ET AL.) 25 AUGUST 1987	
A	US, A, 4,653,851 (PEDERSON ET AL.) 31 MARCH 1987	
A	US, A, 4,602,763 (GAYLIN) 29 JULY 1986	
A	US, A, 4, 441,787(LICHTENBERGER) 10 APRIL 1984	

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

•

Special categories of cited documents:

A

document defining the general state of the art which is not considered to be of particular relevance

E

earlier document published on or after the international filing date

L

document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O

document referring to an oral disclosure, use, exhibition or other means

P

document published prior to the international filing date but later than the priority date claimed

T

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z

document member of the same patent family

Date of the actual completion of the international search

29 NOVEMBER 1994

Date of mailing of the international search report

07 DEC 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

AKM E. ULLAH *AKM E. ULLAH*

Telephone No. (703) 308-4885